

## HYDROTREATMENT OF COAL GASIFICATION LIQUID BY-PRODUCTS WITH A SOLID ACID CATALYST

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KEY WORDS: hydrotreating, gasification, coal tar

### INTRODUCTION

The production of transportation fuels by hydrotreatment of coal tars has been practiced for many years. Coal tars represent an important part of the products of coal gasification units, and as more of these units become operational, a large source of hydrocarbon fuels will be available. Three liquid by-products are produced at the Great Plains Gasification Plant. These include tar oil, crude phenol, and a light naphtha from the rectisol desulfurization unit. Mild gasification processes currently under study produce a liquid product in addition to the char and gas. Conversion of these tars to a transportation fuel requires removal of heteroatoms (nitrogen, sulfur, and oxygen) as well as hydrogenation and cracking of the larger aromatic and aliphatic components.

The production of a high density jet fuel from the Great Plains tar-oil by-product was investigated by hydrogenation with commercial supported bimetallic catalysts (1). The products contained large amounts of cyclohexane components from hydrogenation of the aromatics. For conversion to a gasoline fuel, hydrocracking of polynuclear aromatics in the tars is desired, but addition of hydrogen to single ring aromatics is not required. A new solid acid catalyst has been developed in our laboratory appropriate for the type of hydrotreating needed to produce a gasoline-type fuel with high single ring aromatic content. This catalyst consists of zinc chloride supported on and complexed with silica gel. Coal liquefaction and hydrodesulfurization with this new solid acid catalyst have been recently reported (2,3,4), and its effectiveness for hydrotreating tar samples is discussed in this paper.

### EXPERIMENTAL

A tar oil sample resulting from the gasification of North Dakota lignite (Beulah) had the elemental analysis (5) shown in Table 1. The sample was hydrotreated at 400°C with 1000 psi hydrogen, as previously described (2) for hydrotreatment of liquefaction samples. The product slurry from the reaction of Great Plains tar oil with silica gel-zinc chloride catalyst was transferred into a centrifugation tube and separated into solid and liquid products.

The liquid product was analyzed by GC/FID and GC/MS analyses. Carbon and sulfur emission spectroscopy (GC/MS/AES) was used for the qualitative analyses of the reaction products. The solid product was washed with dichloromethane, vacuum dried, and weighed. Sulfur was analyzed with the Leco instrument, chlorine by the method in Vogel (2).

The second sample was a tar sample produced several years ago in the Grand Forks Energy Technology Center's slagging fixed-bed gasifier from a North Dakota lignite (Indian Head). This sample consisted of the residue after distillation of the light oil components shortly after collection of the tar. The sample was stored in a glass jar without any special precautions against oxidation. The elemental analysis of the sample is given in Table 1.

Hydrotreatment was carried out as described above, and the product distilled under vacuum (2 torr) to 250°C. The distillate was mixed with the appropriate internal standard and analyzed by GC/FID and GC/FTIR/MS/AED, as above. The solid residue was extracted with dichloromethane, and the soluble and insoluble fractions were weighed and analyzed by elemental analysis and infrared spectroscopy.

## RESULTS AND DISCUSSIONS

The reactions of tar oil with a silica gel-zinc chloride catalyst were carried out at 400°C for 3 hours and in the presence of 1000 psig (repressurizations at 1-hour intervals) of molecular hydrogen. The product consisted entirely of distillable material (Table 2). Elemental analysis and mass balance indicated that the dichloromethane-insoluble product was essentially the recovered catalyst. No coke formation was observed.

The original tar oil contained 8% aliphatics, 48% aromatics, and 36% polar compounds (5). Aromatic components consisted of mostly alkylbenzenes and alkyl naphthalenes, but ranged from toluene to pyrene. Polar components consisted of phenolics, as well as dihydroxybenzenes and nitrogen bases. The hydrotreated product contained much fewer polar compounds, with no dihydroxybenzene and no nitrogen bases. The aromatic fraction of the hydrotreated product contained benzene, tetralins, and indanes and their alkyl substituted derivatives as the major components.

Major sulfur components of the original tar oil were alkylthiophenes, benzothiophenes, and a small amount of dibenzothiophene. The very sensitive sulfur emission determination of components by GC/AED showed that all thiophenes and benzothiophenes were removed and only a trace of dibenzothiophene remained in the hydrotreated product.

The dry tar sample was hydrotreated with the silica-gel-supported zinc chloride to give a similar slate of products (Table 2), but with higher average molecular weight. The distillate yield for the dry tar reaction product (82%) represented a substantial improvement over that obtained for the original dry tar.

The distribution of compound types in the original dry tar was 11% aliphatic compounds (alkanes/alkenes), 25% aromatic compounds, and 63% polar compounds. The major aromatic components of the original tar were three- and four-ring compounds. The polar components included a considerable amount of dihydroxybenzene and nitrogen bases.

The aliphatic fraction of the hydrotreated product distillate contained some cycloalkanes, and the distribution of larger alkanes ( $C_{14}$  to  $C_{33}$ ) was essentially unchanged. The distillate still contained small amounts of aromatics such as phenanthrene and pyrene, however the majority of the product components were hydroaromatics, such as tetralin, and alkylbenzenes. The phenolic components consisted of phenol, cresols, and other alkylphenols, but no dihydroxybenzenes were present. No nitrogen components were observed in the distillate.

The major sulfur compound in the original dry tar was dibenzothiophene. The reconstructed sulfur emission chromatogram of the distillate indicated that only a trace of dibenzothiophene remained in the hydrotreated product, and no other organosulfur components were present.

The dichloromethane-soluble fraction of the residue represented 8 wt% of the starting material. This product was analyzed by elemental analysis (C, 77.4; H, 7.9; N, 0.31; S, <0.01; and O, 14.4). The dichloromethane-insoluble fraction was mainly recovered catalyst along with a small amount (6%) of organic material. Approximately 4% of starting material was converted to gas.

#### CONCLUSIONS

The silica gel-zinc chloride catalyst was effective in removing heteroatoms from the coal tars. Dihydroxybenzenes were converted to phenols and aromatics. Polynuclear aromatic components were hydrogenated to hydroaromatics, which were further cracked to smaller compounds, but hydrogenation of single ring aromatics was minimal. Retrograde coking reactions were also minimal. The products obtained were too heavy for gasoline; however, a distillate cut of the hydrotreated products containing components in the benzene to xylene range could be a gasoline additive. Further hydrocracking is need to convert the multi-ring components.

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TABLE 1  
ELEMENTAL ANALYTICAL DATA, WT%

Element	Tar Oil	Tar Residue
Carbon	83.76	83.12
Hydrogen	8.86	7.96
Nitrogen	0.52	0.88
Sulfur	0.39	0.32

TABLE 2  
CATALYTIC HYDROTREATING REACTIONS

Reactants (g)			React. Cond.		Products (%)		
Sample	Cat.	Hydrog. (psi)	Temp. (°C)	Time (hr)	CH <sub>2</sub> Cl <sub>2</sub> -I	CH <sub>2</sub> Cl <sub>2</sub> -S	Dist.
Dry Tar 1.01	SZC 0.5	3 x 1000	400	3	6.0	8.0	82
Tar Oil 2.0	SZC 1.0	3 x 1000	400	3	0	0	98